Magnetic Resonant Mode in the Single-Layer High Temperature Superconductor $Tl_2Ba_2Cu_{6+\delta}$

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An unusual spin excitation mode observed by neutron scattering has inspired numerous theoretical studies of the interplay between charged quasiparticles and collective spin excitations in the copper oxide high temperature superconductors. The mode has thus far only been observed in materials with crystal structures consisting of copper oxide bilayers, and it is notably absent in the single-layer compound $La_{2-x}Sr_xCuO_{4+\delta}$. Neutron scattering data now show that the mode is present in $Tl_2Ba_2Cu_{6+\delta}$, a single-layer compound with $T_c \sim$ 90 K, thus demonstrating that it is a generic feature of the copper oxide superconductors, independent of the layer sequence. This restricts the theoretical models for the origin of the resonant mode and its role in the mechanism of high temperature superconductivity.

Electronic conduction in the copper oxide high temperature superconductors takes place predominantly in structural units of chemical composition CuO_2, in which copper and oxygen atoms form an approximately square planar arrangement. Most theoretical models of high temperature superconductivity are therefore based on a two-dimensional square lattice. In real materials, however, deviations from this simple situation are nearly always present. For instance, buckling distortions of the CuO_2 layers that are found in many copper oxides are thought to have a significant influence on the electronic structure and on the superconducting transition temperature $\mathrm{T_c}$. Interlayer interactions in materials with closely spaced CuO_2 layers (forming bi- or trilayer units) or additional copper oxide chains in the crystal structure present further complications whose influence on the superconducting properties remains a subject of debate. Experiments on $Tl_2Ba_2CuO_{6+\delta}$, a material with unbuckled, widely spaced CuO_2 layers and a maximum $\mathrm{T_c}$ around 90 K, have therefore played a pivotal role in resolving some issues central to our understanding of these materials (*1*, *2*). We report inelastic neutron scattering measurements of $Tl_2Ba_2CuO_{6+\delta}$ near optimum doping ($\mathrm{T_c} \sim 90$ K) that provide evidence of a sharp magnetic resonant mode below $\mathrm{T_c}$.

A resonant spin excitation of this kind has been extensively characterized by neutron scattering in the bilayer copper oxide $YBa_2Cu_3O_{6+\delta}$ (*3*–*5*) and was recently also observed in $Bi_2Sr_2CaCu_2O_{8+\delta}$, another bilayer compound (*6*, *7*). At all doping levels, strong line shape anomalies of this collective spin excitation below $\mathrm{T_c}$ bear witness to a substantial interaction with charged quasiparticles. Conversely, anomalies in the quasiparticle spectra observed by photoemission (*8*, *9*), optical conductivity (*10*–*13*), tunneling (*13*, *14*), and Raman scattering (*15*) techniques have been interpreted as evidence of coupling to the neutron mode. In the copper oxides (as well as some heavy fermion materials, where similar observation have been made (*16*) the correspondence between anomalous features in the spectra of spin and charge excitations has stimulated spin fluctuation based pairing scenarios (*9*, *11*, *16*) which are, however, still controversial (*17*–

19). Other theories of high temperature superconductivity also rely on the resonant mode (*20*). It is therefore of great interest to establish whether the resonant spin excitation is a general feature of the various crystallographically distinct families of superconducting copper oxides. The failure to detect such an excitation in the single-layer compound $La_{2-x}Sr_xCuO_{4+\delta}$, despite much experimental effort (*21*), has hampered a unified phenomenology of the copper oxides, and the prospect that the mode could be a spectral feature specific to bilayer materials has cast a cloud over models in which spin excitations play a central role. The result of our experiment on single-layer $Tl_2Ba_2CuO_{6+\delta}$ (whose $T_c \sim 90$ K is closely similar to that of optimally doped $YBa_2Cu_3O_{6+\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$) implies that strong magnetic interactions between closely spaced CuO_2 layers are not required for the formation of the resonant mode. The different form of the spin excitation spectrum of $La_{2-x}Sr_xCuO_{4+\delta}$ may be due to the proximity of a competing instability (*22*) that could also be responsible for the anomalously low $T_c \leq 40$K.

Inelastic magnetic neutron scattering measurements on conventional triple axis or time-of-flight spectrometers require high quality copper oxide single crystals with volumes of at least 1 cm^3, which are only available for the $La_{2-x}Sr_xCuO_{4+\delta}$ and $YBa_2Cu_3O_{6+\delta}$ families. Due to advances in focusing techniques that improve the neutron beam delivery onto small samples, experiments on single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ with an order of magnitude smaller volumes have recently become feasible (*6, 7*). Unfortunately, the crystal growth of the Tl- and Hg-based copper oxide superconductors (which include the only known single-layer compounds with T_c of order 90 K) has suffered from severe technical difficulties, chief among them the toxicity of some of the constituents. With typical crystal volumes well below 1 mm^3, inelastic neutron scattering on these compounds has thus far appeared hopeless. We have overcome these difficulties by synthesizing about 300 relatively large (0.5–3 mm^3) single crystals of $Tl_2Ba_2CuO_{6+\delta}$ through a CuO-rich flux technique (*23*), and co-aligning them in a mosaic of total volume 0.11 cm^3 using Laue x-ray diffraction (Fig. 1A). The crystallographic axes of the individual crystals

in the array were aligned with an accuracy of about 1.5° (Fig. 1C). Before alignment, the magnetic susceptibilities of all crystals were measured as a function of temperature (typical data are shown in Fig. 1B). The mean T_c (onset) of the individual crystals used in the array was 92.5 K, with a standard deviation of 2 K.

Compared to previous neutron scattering experiments on much larger crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$, the background from the Al plates and the adhesive holding the multicrystal array (Fig. 1A) was significantly enhanced, while the signal amplitude is substantially smaller due to the single-layer structure (see below). In order to compensate for this reduction in signal-to-background ratio, counting times of up to 5 hours per data point had to be used. Of particular interest was the energy range around 40 meV, where the resonant mode was observed in both $YBa_2Cu_3O_{6+\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$ near optimum doping. In these two materials, the mode manifests itself in a sharply enhanced intensity around the in-plane wave vector $\mathbf{Q}_{\mathrm{AF}} = (\frac{1}{2}, \frac{1}{2})$ that is present only below T_c; when the doping is reduced, magnetic intensity is observed also above T_c. (The components of the wave vector are denoted as $\mathbf{Q} = (H, K, L)$ and given in units of the reciprocal lattice vectors $a^* = b^* = 1.62$ Å^{-1} and $c^* = 0.27$ Å^{-1} of the tetragonal structure.) As a function of the wave vector component L perpendicular to the CuO_2 layers, one observes an intensity modulation due to strong interlayer interactions within a bilayer unit (*3–7*). As the $Tl_2Ba_2CuO_{6+\delta}$ are much further apart and hence much more weakly interacting, it is expected that this modulation is absent, and that the magnetic intensity is independent of L except for a slow decrease with increasing L due to the magnetic form factor. Note that the absence of the bilayer modulation goes along with a factor-of-two reduction in signal amplitude, which is further compounded by the lower density of CuO_2 planes in the $Tl_2Ba_2CuO_{6+\delta}$ structure.

The constant-energy scans (Fig. 2) indeed exhibit this characteristic signature, albeit at an energy of 47 meV that is somewhat larger than 40 meV, the mode energy in the optimally doped bilayer compounds; constant-energy scans around 40 meV were featureless (Fig. 2D). These

data were taken on two different spectrometers with different final energies, with identical results. Above T_c, the scans show a featureless background that gradually decreases in an energy- and **Q**-independent fashion as the temperature is lowered. In the superconducting state, a sharp peak centered at $\mathbf{Q}_{\rm AF}$ appears on top of this background. As expected for magnetic scattering that is uncorrelated from layer to layer, the peak intensities measured at two inequivalent L-positions ($L = 10.7$ and 12.25, respectively) are identical within the errors. The identification of this peak with the magnetic resonant mode is further supported by comparing constant-**Q** scans at $\mathbf{Q} = \mathbf{Q}_{\rm AF}$ above and below T_c. The difference signal shows a peak that is resolution limited in energy (Fig. 3), in agreement with observations in optimally doped $YBa_2Cu_3O_{6+\delta}$.

Constant-energy scans taken at different temperatures were fitted to Gaussian profiles (Fig. 2). The best overall fit was provided by an intrinsic **Q**-width of 0.23 ± 0.05 Å^{-1} (full width at half maximum). The data were subsequently refitted with the **Q**-width kept fixed in order to reduce scatter, and the peak amplitude thus extracted as a function of temperature (Fig. 4). There is some indication of a broad peak centered around $\mathbf{Q}_{\rm AF}$ even above T_c, as observed in underdoped $YBa_2Cu_3O_{6+\delta}$ (*3-5*), but this is well within the experimental error. Based on a calibration measurement of acoustic phonons (Fig. 1D), the spectral weight of the mode (that is, the energy-integrated intensity) at $\mathbf{Q}_{\rm AF}$ is determined as $0.7 \pm 0.25\ \mu_B^2$, which corresponds to $0.02 \pm 0.007\ \mu_B^2$ when averaged over the entire Brillouin zone. Both the **Q**-width and the absolute spectral weight per CuO_2 plane of the peak observed in $Tl_2Ba_2CuO_{6+\delta}$ are identical within the errors to those of the resonant mode measured in $YBa_2Cu_3O_7$ (*4, 24*), as are its dependence on energy and temperature. Although for $Tl_2Ba_2CuO_{6+\delta}$ the experimental information is much more limited at this time than for the latter material (large crystals of which have been studied for more than a decade), the cumulation of independent matching features allows us to infer with confidence a common origin of both phenomena. Other possible explanations of the observations in $Tl_2Ba_2CuO_{6+\delta}$ (such as phonon anomalies) would require an implausible

coincidence, especially since above T_c both the raw constant-energy scans (Fig. 2B) and the raw constant-**Q** scans around 47 meV (Fig. 3A) are featureless.

It is interesting to note that the resonant modes of both $YBa_2Cu_3O_7$ and $Tl_2Ba_2CuO_{6+\delta}$ are resolution limited in energy whereas a significant broadening is found in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (*6, 7*). As even small concentrations of impurities systematically introduced into $YBa_2Cu_3O_7$ broaden the mode considerably (*24, 25*), the broadening in $Bi_2Sr_2CaCu_2O_{8+\delta}$ was attributed to disorder. The sharpness of the mode observed in optimally doped $Tl_2Ba_2CuO_{6+\delta}$ appears to imply that disorder effects are minimal in this material, a surprising finding in view of the fact that $Tl_2Ba_2CuO_{6+\delta}$ (in contrast to $YBa_2Cu_3O_7$) is nonstoichiometric. It also means that the model of Refs. (*11, 12*), though qualitatively correct in predicting the presence of a resonant spin excitation in $Tl_2Ba_2CuO_{6+\delta}$, needs to be re-evaluated in view of the fact that the experimentally determined peak width is much smaller than predicted on the basis of the optical conductivity data. The mode energy found in $Tl_2Ba_2CuO_{6+\delta}$ notably exceeds the ones in both $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$. This is in agreement with models according to which the resonant mode is a collective excitation pulled below the quasiparticle pair production continuum by exchange interactions (*8, 9, 26–29*). The lower mode energy in the bilayer materials could thus be a consequence of the strong interactions between the two CuO_2 layers that form a bilayer unit (*26–29*), assuming that the energy gap and hence the pair production threshold are identical in materials with identical T_c as indicated by electronic Raman scattering results (*30*).

The most important implication of the findings reported here regards the unified phenomenological picture recently developed for spin and charge spectroscopies of the copper oxides (*8–14*). The spectral anomalies that have been interpreted as evidence of coupling to the collective spin excitation are also present in optical conductivity (*31*) and tunneling (*32*) data on single-layer $Tl_2Ba_2CuO_{6+\delta}$, and equally pronounced as in analogous data on bilayer materials. If the mode had turned out to be absent (or its spectral weight substantially diminished) in

$Tl_2Ba_2CuO_{6+\delta}$, this general approach would have become untenable. It is now time to further refine the description of the coupled spin and charge excitations in the cuprates, and to fully evaluate its implications for the mechanism of high temperature superconductivity.

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Figure Captions

Fig. 1. (A) Photograph of the array of co-oriented $Tl_2Ba_2CuO_{6+\delta}$ single crystals. The crystals are glued onto Al plates only two of which are shown for clarity. (B) Typical diamagnetic shielding curves measured by SQUID magnetometry on individual crystals. (C) Rocking curve of the entire multicrystal array around the (1,1,0) Bragg reflection. The line is a Gaussian with a full width at half maximum of 1.5°. (D) Constant-energy scan along $\mathbf{Q} = (2, 2, L)$ at excitation energy 3.1 meV and temperature 100 K, showing two counterpropagating transverse acoustic phonons. The wave vector **Q** is given in reciprocal lattice units (r.l.u.). The data were taken at the 2T1 triple axis spectrometer at the Orphée research reactor in Saclay, France, with a pyrolytic graphite (PG) monochromator and a PG analyser set at the (002) reflection, and a fixed final energy of 14.7 meV. Three PG filters were inserted into the neutron beam in order to eliminate higher order contamination. The asymmetry of the profile is a resolution effect, and the solid line shows the result of a numerical convolution of a standard acoustic phonon dispersion with the spectrometer resolution.

Fig. 2. (A,B) Constant-energy scans along $\mathbf{Q} = (H, H, L)$ with $L = 10.7$ at an energy of 47.5 meV, taken on 2T under the same conditions as the data of Fig. 1D. (C,D) Constant-energy scans at 47 and 40 meV, respectively, taken on the IN22 spectrometer at the Institut Laue-Langevin in Grenoble, France, with a PG (002) monochromator and analyser and fixed final energy 30.5 meV. The wave vector **Q** is given in reciprocal lattice units (r.l.u.). The background revealed by scans above $\mathrm{T_c}$ (panel B) remained constant upon lowering the temperature except for a **Q**-independent scale factor. The lines in the upper panels are the results of fits as described in the text.

Fig. 3. Constant-**Q** scans at $\mathbf{Q} = (0.5, 0.5, 12.25)$ taken under the same conditions as the data of Fig. 1D. (A) Raw data at $\mathrm{T} = 99\mathrm{K}$ ($> \mathrm{T_c}$) and $\mathrm{T} = 27$ K ($< \mathrm{T_c}$). (B) Difference between the two scans of panel A. The line is a Gaussian profile whose width equals the experimental

energy resolution.

Fig. 4. Temperature dependence of the magnetic intensity extracted from fits to constant-energy scans at energy 47.5 meV around the in-plane wave vector $\mathbf{Q_{AF}} = (1/2, 1/2)$ (Fig. 2). The data were taken on two different spectrometers (2T and IN22) at different components of the out-of-plane wave vector L.